

**CRACKING OR PYROLYSIS.** Cracking on a very large scale has been used for over 50 years to produce carbon black. This very useful substance is discussed in Chap. 8. Olefins and diolefins are made, mainly by catalytic cracking of various hydrocarbons, and the scale is very large. The most important product, produced at a rate of  $12.7 \times 10^9$  kg/year is ethylene, with by-product propylene produced at a rate of  $5.9 \times 10^9$  kg/year. It is made by steam cracking at 760 to 870°C with very short residence time. Quenching, followed by compression to 3.5 MPa, precedes separation processes. Ethylene, propylene, butadiene, and aromatics are all found in the product. Currently low-molecular-weight hydrocarbons (natural gas) are the preferred feedstocks, but increasing amounts will be made from heavy hydrocarbons.

*Acetylene* is made by cracking and is used in substantial quantities. Its manufacture is discussed in Chap. 7.

$\alpha$ -Olefins<sup>8</sup> for use in manufacturing detergents can be made by cracking heavy paraffins, but many  $\alpha$ -olefins are made by oligomerization of lighter hydrocarbons, such as ethylene, and others by the Alfol process or the Ziegler process involving the use of trialkylaluminum.  $\alpha$ -Olefins in the range of 12 to 18 carbon atoms are particularly desired for detergent alkylate because of their ready biodegradability.

**DEHYDRATION.** Dehydration is commonly used in the production of ethers by the dehydration of alcohols. Much diethyl ether is made by dehydrating ethyl alcohol with sulfuric acid as the dehydrating agent. Vapor phase dehydration over catalysts such as alumina is also practiced. Hydration of olefins to produce alcohols, usually over an acidic catalyst, produces substantial quantities of ethers as by-products. The reverse reaction, ethers to alcohols, can be accomplished by recycling the ethers over a catalyst.

**ESTERIFICATION<sup>9</sup> WITH INORGANIC ACIDS.** A variety of solvents, monomers, medicines, perfumes, and explosives are made from esters of nitric acid. Glycerol trinitrate, pentaerythritol tetranitrate (PETN), glycol dinitrate, and cellulose nitrate are discussed in Chap. 22.

**ESTERIFICATION<sup>10</sup> OF ORGANIC ALCOHOLS AND ACIDS.** Ethyl acetate has been an important solvent, particularly for lacquers, for many years. It is usually sold as an 85% solution and  $10.6 \times 10^9$  kg was sold in the United States in 1980. Other esters made on a large scale are *n*-butyl acetate ( $53.7 \times 10^6$  kg/year) and isobutyl acetate ( $36.6 \times 10^6$  kg/year). Ester synthesis is relatively simple. The alcohol and an acid are heated together in the presence of a little sulfuric acid, and the reaction is driven to completion by removing the products as formed (usually by distillation) and employing an excess of one of the reagents. In the case of ethyl acetate, esterification takes place in a column which takes a ternary azeotrope (bp 70.2°C; 82.2% EtAc, 8.4% alcohol, 9% water) overhead. Alcohol can be added to the condensed overhead liquid to wash out the alcohol, which is then rectified and returned to the column to react.

Amyl, butyl, and isopropyl acetates are all made from acetic acid and the appropriate alcohols. All are useful lacquer solvents and their slow rate of evaporation (compared to acetone or ethyl acetate) prevents the surface of the drying lacquer from falling below the dew point, causing condensation on the film and a mottled surface appearance. This phenomenon

<sup>8</sup>Freitas and Gum, Shell's Higher Olefins Process, *Chem. Eng. Prog.* **75** (1) 73 (1979).

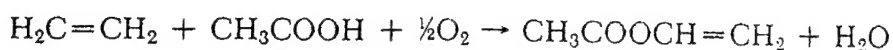
<sup>9</sup>Groggins, op. cit., p. 694.

<sup>10</sup>Groggins, op. cit., p. 727; Lowenheim and Moran, *Industrial Chemistry*, 4th ed., Wiley-Interscience, New York, 1975, p. 350.

is known as "blushing." Other esters of importance are used in perfumery and in plasticizers. These include methyl salicylate, methyl anthranilate, diethyl-, dibutyl-, and di 2-ethylhexyl-phthalates.

Unsaturated vinyl esters for use in polymerization reactions are made by the esterification of olefins. The most important ones are vinyl esters: vinyl acetate ( $929 \times 10^6$  kg/year), vinyl chloride ( $2954 \times 10^6$  kg/year), acrylonitrile ( $327 \times 10^6$  kg/year), and vinyl fluoride. The addition reaction may be carried out in either the liquid, vapor, or mixed phases. The choice depends upon the properties of the acid. Care must be taken to reduce the polymerization of the vinyl ester produced.

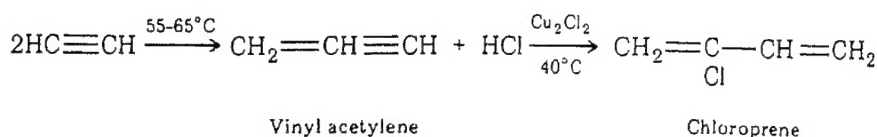
*Vinyl acetate*<sup>11</sup> is manufactured by reacting ethylene with acetic acid in the vapor phase over a supported palladium catalyst.



The reaction is conducted in a fixed bed tubular reactor and is highly exothermic. With proper conditions, the only significant by-product is  $\text{CO}_2$ . Enough heat is recovered as steam to perform the recovery distillation. Reaction is at 175 to 200°C under a pressure of 475 to 1000 kPa. To prevent polymerization, an inhibitor such as diphenylamine or hydroquinone is added. Units for this process are quite large, some producing  $50 \times 10^6$  kg/year.

An older process reacts acetylene with acetic acid in the liquid phase. Most vinyl acetate is now produced from ethylene.

*Chloroprene*, the monomer used in making neoprene, is a chlorovinyl ester of hydrochloric acid. It can be prepared by polymerizing acetylene to vinyl acetylene using a weak solution containing  $\text{NH}_4\text{Cl}$ ,  $\text{Cu}_2\text{Cl}_2$ , and  $\text{KCl}$  as catalyst. The off-gas from the reactor has its water condensed out and is then fractionated. Aqueous hydrochloric acid at 35 to 45°C is then reacted with the vinyl acetylene in the presence of  $\text{Cu}_2\text{Cl}_2$  to give chloroprene (2-chloro-1,3-butadiene):



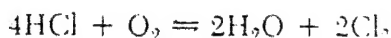
Esters of allyl alcohol, e.g., diallyl phthalate, are used as bifunctional polymerization monomers. They can be prepared by simple esterification of phthalic anhydride with allyl alcohol. Several acrylic esters, such as ethyl or methyl acrylates, are also widely used and can be made from acrylic acid and the appropriate alcohol. The esters are more volatile than the corresponding acids.

**HALOGENATION AND HYDROHALOGENATION.**<sup>12</sup> Liquid and vapor halogenations have been studied and all produce mixes of products. The casual rule "you always get everything" seems to apply generally, and the greatest problem is often to direct the course of the reaction toward a preponderance of the desired product. It is frequently equally difficult to separate the multicomponent mix obtained.

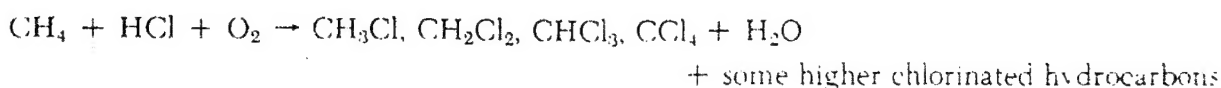
<sup>11</sup> *Hydrocarbon Process.* 60 (11) 234 (1981).

<sup>12</sup> Groggins, op. cit., p. 204; Belohlar and McBee, Halogenation, *Ind. Eng. Chem.*, annual review supplement, 1962, p. 77.

Most chlorinations produce HCl as a by-product, and for years a method was searched for to make this useful for chlorinations. The Deacon process was most frequently suggested. It employs the following reaction:



Because this is an equilibrium reaction not greatly favoring the right-hand side, and because most of the components are highly corrosive to common materials of construction, this reaction has never been really successful commercially. The reaction, however, can be used and driven to completion by use of the *oxychlorination* procedure. This reacts the chlorine with a reactive substance as soon as it is formed, thus driving the reaction to completion. Consider the oxychlorination of methane:



This chlorination can be made with  $\text{Cl}_2$ , but a mole of HCl will be produced for every Cl introduced, and this must be disposed of to prevent environmental pollution. By-product HCl from other operations is frequently available at low cost. Cuprous and cupric chlorides, along with some potassium chloride as a molten salt catalyst, will speed up the reaction. Figure 38.6 shows a flowchart for a commercial installation. All waste chloro compounds are recirculated and consumed leaving only nonpolluting  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  as effluents. The chloromethanes enjoy wide use and considerable production.

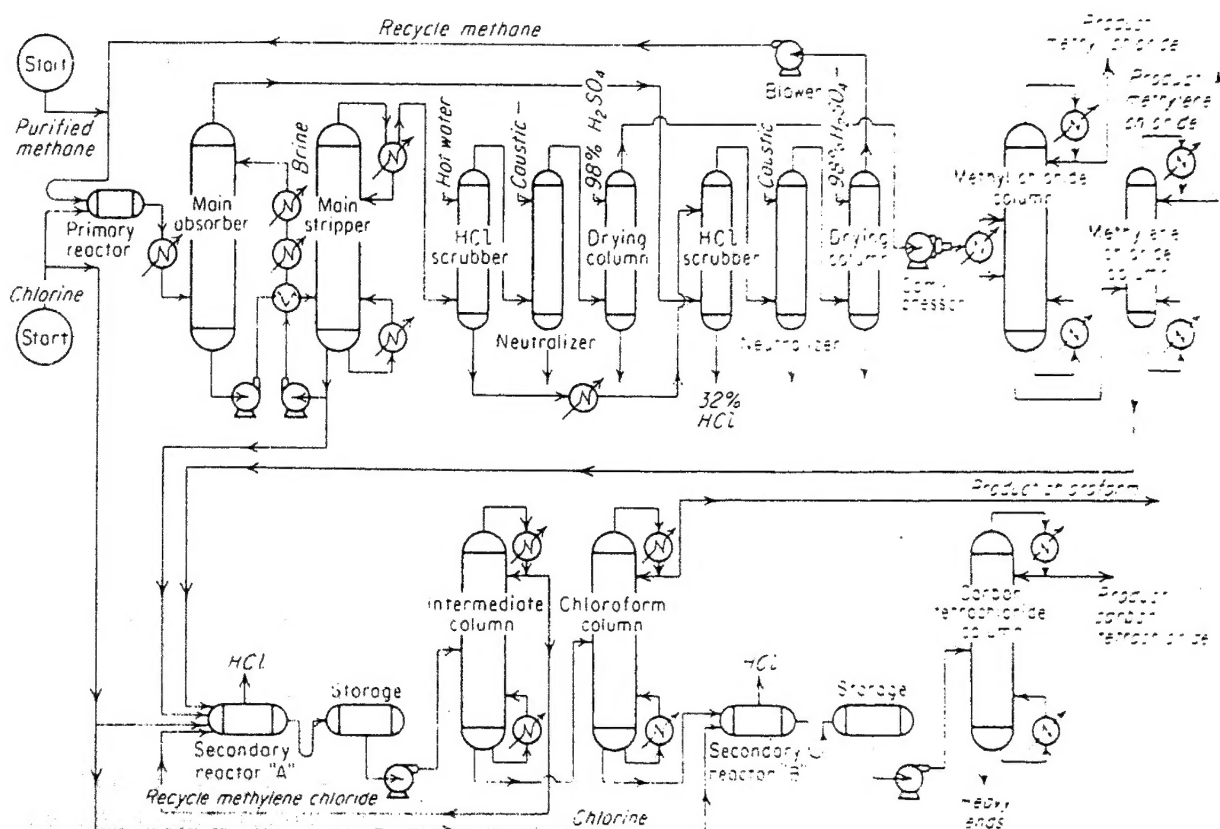
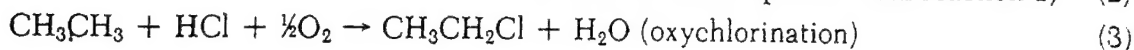
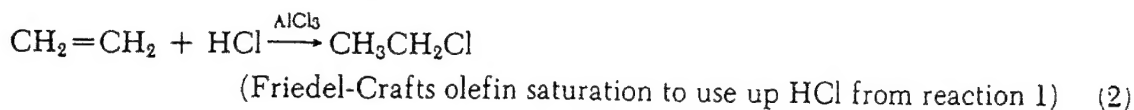
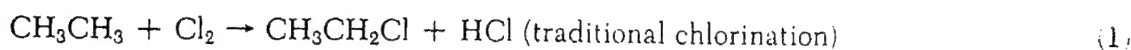


Fig. 38.6. Flowchart for chlorinating methane. The HCl scrubbers may be made of Karbate carbon (Petroleum Refiner.)

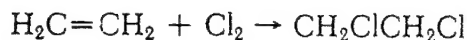
Individual Chloromethane	Production in 10 <sup>6</sup> kg/year (for 1980)	Uses, percent
Methyl chloride, CH <sub>3</sub> Cl	177	Silicones 57, TML 9, methyl cellulose 4
Methylene chloride, CH <sub>2</sub> Cl <sub>2</sub>	254	Paint remover 30, aerosol propellant
	227 (1982)	20, degreaser 10
Chloroform, CHCl <sub>3</sub>	183	Fluorocarbons 90, miscellaneous
Carbon tetrachloride, CCl <sub>4</sub>	322	Fluorocarbons 95, fumigant, degreasing

In Fig. 38.6, the chlorine and new and recycled methane are charged in the ratio 0.6/1.0. In the reactor, the temperature is maintained at 340 to 370°C. The chlorine conversion is total, and the methane conversion around 65 percent. Ignition is avoided by using narrow channels and high velocities in the reactor. The reaction product contains chlorinated hydrocarbons in the proportions: CH<sub>3</sub>Cl, 6; CH<sub>2</sub>Cl<sub>2</sub>, 3; CHCl<sub>3</sub>, 1; CCl<sub>4</sub>, 0.25. There are also unreacted methane, HCl, Cl<sub>2</sub>, and heavier chlorinated products. Secondary chlorinations take place at ambient temperature in a light-catalyzed reactor A which converts methylene chloride to chloroform, and in reactor B, which converts chloroform to carbon tetrachloride. By changing reagent ratios, temperatures, and recycling ratios, it is possible to vary the product mix somewhat to satisfy changing market demands.

**Ethane Chlorination.**<sup>13</sup> Ethane can be chlorinated under conditions very similar to those for methane to yield mixed chlorinated ethanes. Ethyl chloride (demand  $214 \times 10^6$  kg in 1979) has been used mainly (90 percent) for making tetraethyl lead, and can be made by any one of three methods:



**Ethylene Dichloride.**<sup>14</sup> When chlorine is added to olefins such as ethylene, many and mixed derivatives are formed; ethylene dichloride, dichloroethylene, trichloroethylene, tetrachloroethane, chloromethanes, and higher chloromethanes all form. Other halogens produce similar mixtures. With care, good yields of the desired product are possible. Ethylene dichloride, for example, can be prepared with 96 percent yield as follows:



Ethylene bromide vapor (as catalyst) and Cl<sub>2</sub> gas meet a stream of ethylene in a chlorinating tower at 40 to 50°C. The tower has a partial condenser to strip out the ethylene bromide catalyst for recirculation, then a condenser-separator which separates unreacted ethylene for

<sup>13</sup>Shell Development, U.S. Patent 2,246,082; Lowenheim and Moran, op. cit., p. 371; Sittig, op. cit., p. 304; *Chem. Eng.* 81 (13) 114 (1974).

<sup>14</sup>Lowenheim and Moran, op. cit., p. 392.

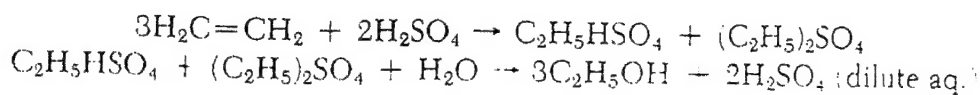
recycle. Fractionation separates the higher-boiling materials. Oxychlorination can also be used to produce mixed products as in the case of methane. Ethylene dichloride is used in making ethylenediamine and Thiokol rubber.

*Perchloroethylene* (tetrachloroethylene,  $\text{CCl}_2=\text{CCl}_2$ )<sup>15</sup> is used for textile cleaning and vapor degreasing to the extent of  $327 \times 10^6$  kg/year in 1981. 1,1,1-Trichloroethylene ( $253 \times 10^6$  kg/year in 1981) is usually made in the same apparatus or as a coproduct. Both chlorination and oxychlorination are used to supply the reagents needed. The reactions follow the same pattern as those for ethane and methane chlorination. Temperatures, pressures, and reagent ratios are somewhat different, however. *Trichloroethane* is used for vapor and cold degreasing, 62 percent; in adhesives, 12 percent; in aerosols, 10 percent; and in electronics, 6 percent.

Chlorinolysis is used to dispose of unwanted chlorinated hydrocarbons with one to three carbon atoms. These are reacted at high temperature ( $700^\circ\text{C}$ ) with chlorine to yield mixed carbon tetrachloride and perchloroethylene. These can be recycled to give other chlorinated products if desired. When trichloroethylene is made from acetylene, it can be carried through chlorination to pentachloroethane, then treated with milk of lime to form perchloroethylene, but this is rarely profitable.

**HYDRATION AND HYDROLYSIS.**<sup>16</sup> Synthetic ethyl alcohol ( $5.0 \times 10^5$  kg used in 1982) is generally thought of as the product of fermentation, but most is made by hydration of ethylene. Government interference in the market place and the demand for production from the huge surplus of grain have not changed the economics: alcohol from ethylene is purer and cheaper.

An older process dissolves ethylene in sulfuric acid to form ethyl sulfate, then hydrolyzes this to form ethanol. There is always some by-product ether which can be either sold or recirculated.



The yield is 90 percent with 5 to 10% as  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ . A direct hydration method Fig. 38.7

<sup>15</sup>*Hydrocarbon Process.* 60 (11) 195 (1981).

<sup>16</sup>Lowenheim and Moran, op. cit., p. 356; Groggins, op. cit., p. 750.

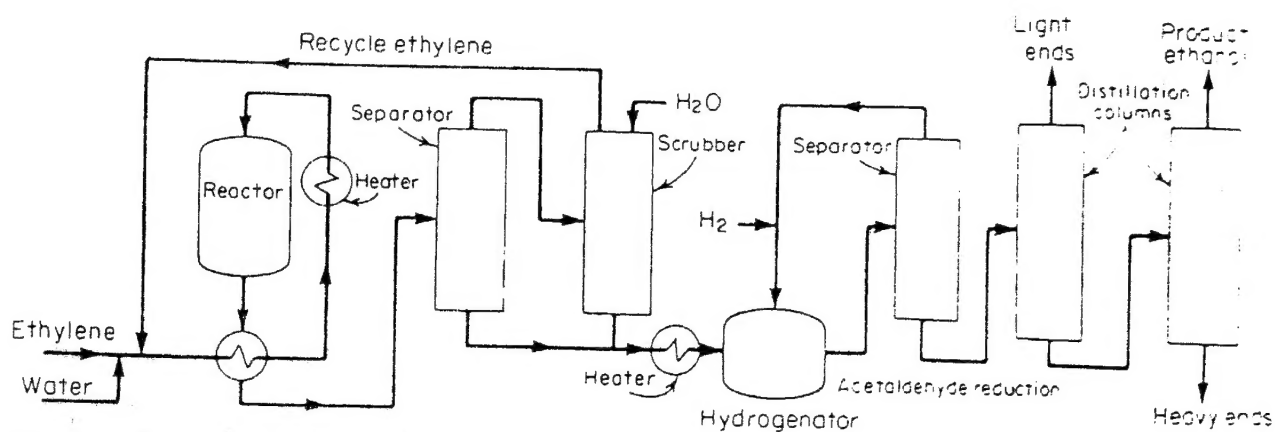
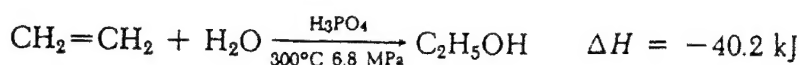


Fig. 38.7. Flowchart for synthesis of ethyl alcohol from ethylene by direct hydration.

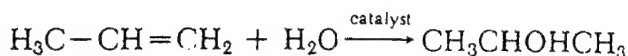
is currently favored for over 85 percent of production:



$\text{H}_3\text{PO}_4$  catalyst is used at  $300^\circ\text{C}$  and 6.8 MPa which gives a yield of 92 percent; conversion per pass is 4 to 25 percent, depending on the activity of the catalyst used. Ethylene and water are combined with a recycle stream in the ratio ethylene/water = 1/0.6 (mole ratio), a furnace heats the mixture to  $300^\circ\text{C}$ , and the gases react over the catalyst of phosphoric acid absorbed on diatomaceous earth. Unreacted reagents are separated and recirculated. By-product acetaldehyde is hydrogenated over a catalyst to form more alcohol.

Primarily because of political pressure and government subsidies, the production of fermentation alcohol is growing astronomically. Much ethanol and methanol is finding its way into fuel mixtures, commonly known as gasohol. Brazil is conducting a major experiment in using pure alcohol as motor fuel. The results of these experiments remain economically unclear. Fermentation alcohol is discussed in Chap. 31 along with procedures for making absolute (anhydrous) alcohol. The maximum alcohol content obtainable by simple distillation is 95%, and this will not mix with gasoline. Anhydrous alcohol will mix with gasoline, but the addition of a small amount of moisture will cause it to separate out. It will absorb moisture from the air. Despite all these objections, it seems probable that alcohols will ultimately become fuels in substantial volume.

*Isopropyl alcohol*<sup>17</sup> is a widely used ( $8.4 \times 10^8$  kg in 1981) and easily made alcohol, the first petrochemical. It is used in making acetone, 23 percent (this use is falling because of competition from the cumene to phenol and acetone process—current use is probably considerably less than this); process solvent, 10 percent; cosmetics, 8 percent; and chemical derivatives, 6 percent. Four processes compete: (1) a sulfuric acid process similar to the one described for ethanol hydration, (2) a gas-phase hydration using a fixed-bed-supported phosphoric acid catalyst, (3) a mixed-phase reaction using a cation exchange resin catalyst, and (4) a liquid-phase hydration in the presence of a dissolved tungsten catalyst. Reactions 2, 3, and 4 are all essentially direct hydration processes.



Per pass conversions vary from a low of 5 to a high of 70 percent for the gas-phase reaction. Reaction 1 is certainly obsolete because of the expense of using sulfuric acid and its pollution problems. The other processes are competitive, nonpolluting, and dependent on catalyst life and recycling problems for their economic life.

Secondary butanol can be made by processes similar to those described for ethylene and propylene.

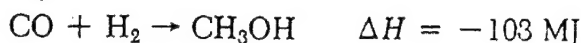
**HYDROGENATION, DEHYDROGENATION.** Hydrogenation yields many useful chemicals, and its employment is increasing spectacularly, particularly in the petroleum refining industry. The cost of hydrogen is a major factor in restricting growth. For the production of hydrogen, see Chap. 7. Besides saturating double bonds, hydrogenation can be used to eliminate other elements from a molecule. These elements include oxygen, nitrogen, halogens, and particu-

<sup>17</sup>Onoue, Mizutani, Akiyama, and Izumi, Hydration with Water, *CHEMTECH* 8 (7) 432 (1978); *Hydrocarbon Process.* 60 (11) 182–184 (1981).



larly sulfur. Cracking in the presence of hydrogen is particularly effective in desulfuring heavy petroleum fractions, thus producing high-quality products. Although occasionally hydrogen for a reaction is provided by donor molecules and a few older reactions use hydrogen generated by acid or alkali acting upon a metal, gaseous hydrogen is the usual hydrogenation reagent. Hydrogenations are generally carried out in the presence of a catalyst and under elevated temperature and pressure. Noble metals, nickel, copper, and various metal oxide combinations are the common catalysts. Lower pressures and higher temperatures favor dehydrogenation, but the catalysts used are the same as for hydrogenation. Ammonia, not generally thought of as a petrochemical but certainly an important one, is discussed in Chap. 18.

Methanol<sup>18</sup> is manufactured by procedures very similar to those used for ammonia, using CO and H<sub>2</sub> from synthesis gas as raw materials and a copper-based catalyst (Fig. 38.8):



Usage is large,  $3.30 \times 10^9$  kg in 1982, and likely to become larger, perhaps huge. There is great interest in this material as an all-purpose fuel. Its production from biomass is being carefully studied, and the literature is full of speculative ideas.<sup>19</sup> Like ammonia, recent years have seen the usual synthesis pressure fall from 8 MPa to around 3 MPa. This has made the use of centrifugal compressors possible and resulted in considerable savings. New catalysts have helped push up the conversion. The older, high-pressure processes used zinc-chromium catalysts, but the low-pressure units use highly active copper catalysts; lately liquid-entrained micron-sized catalysts have been developed which can convert as much as 25 percent per pass. Contact of the synthesis gases with hot iron catalyzes competing reactions and also forms volatile iron carbonyl which fouls the copper catalyst. Some reactors are lined with copper. Table 38.7 shows the effect of temperature and pressure upon the methanol synthesis.

Synthesis gas is made and its composition adjusted as discussed in Chap. 6. Economical preparation of the gas is vitally important, for its cost constitutes nearly 75 percent of the final cost of the methanol. Both high- and low-pressure partial oxidation processes are used.

<sup>18</sup>Supp, Technology of Lurgi's Low Pressure Methanol Process, *CHEMTECH* 3 (7) 430 (1973).

<sup>19</sup>Frank, Methanol: Emerging Uses, New Syntheses, *CHEMTECH* 12 (6) 358 (1982); Haggin, Methanol: Future Fuel for Electric Utilities? *Chem. Eng. News* 60 (29) 41 (1982); McCallum et al., Alcohol Fuels for Highway Vehicles, *Chem. Eng. Prog.* 78 (7) 52 (1982).

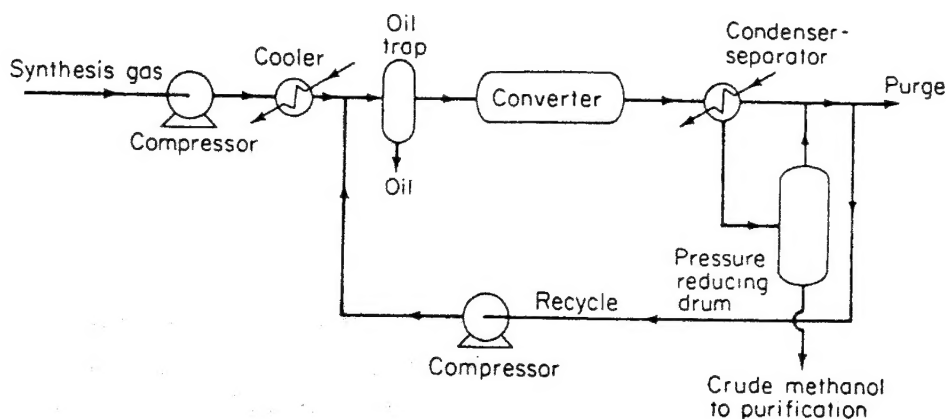


Fig. 38.8. Flowchart for the conversion of synthesis gas to methanol.

**Table 38.7** Methanol Synthesis Data

Equilibrium Constants		Effect of Pressure on Equilibrium Conversion	
Temperature, °C	$K_p$	Pressure, MPa at 300°C	Percent Conversion to Liquid Methyl Alcohol in One Pass
200	$1.7 \times 10^{-2}$	100	
300	$1.3 \times 10^{-4}$	500	8.0
400	$1.1 \times 10^{-5}$	1000	24.2
		2000	48.7
		3000	62.3

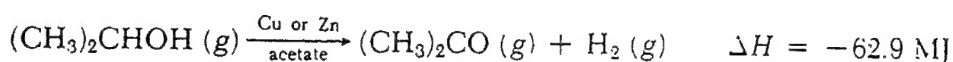
SOURCES: *Ind. Eng. Chem.* 32 147 (1940); Goldstein and Waddams, *Petroleum Chemicals Industry*, Spon, 1967, p. 55; cf. ammonia synthesis data and equipment in Chap. 18.

Because the catalyst is sensitive to sulfur, the gases are purified by one of several sulfur-removing processes, then are fed through heat exchangers into one of two types of reactors. With bed-in-place reactors, steam at around 4.5 MPa, in quantity sufficient to drive the gas compressors, can be generated. A tray-type reactor with gases introduced just above every bed for cooling offers more nearly isothermal operation but does not give convenient heat recovery. Figure 38.8 shows a flowchart for a Lurgi low-pressure plant. Pressure is 5 to 8 MPa, and the reactor temperature is 250 to 260°C. High- and low-boiling impurities are removed in two columns and the unreacted gas is recirculated. With changing market swings, some methanol plants have been converted into ammonia plants (and vice versa) without major change.

*Styrene* is produced from ethylbenzene by dehydrogenation; a flowchart is given in Fig. 36.3.

Many lower molecular weight aliphatic *ketones*<sup>20</sup> are made by dehydration of alcohols. Acetone, methyl ethyl ketone, and cyclohexanone can be made in this fashion. The production of cyclohexanone is considered later in this chapter under caprolactam.

Acetone is the ketone used in largest quantity ( $8.1 \times 10^6$  kg in 1981) and virtually all of it is now produced as a by-product of the manufacture of phenol via cumene. Manufacture from isopropanol is by the reaction:



This reaction takes place at around 200 kPa and 350°C giving 85 to 90 percent conversion. Purification by distillation follows. Because of competition and decreasing acetone demand, manufacture from isopropanol has fallen upon hard times and all U.S. plants are currently shut down. In periods of more normal business activity they make about one-third of the acetone used.

**NITRATION.**<sup>21</sup> Nitration offers a method of making unreactive paraffins into reactive substances without cracking. Because nitric acid and nitrogen oxides are strong oxidizing agents, oxidation always accompanies nitration. Aromatic nitrations have been important

<sup>20</sup>Ketones, *Hydrocarbon Process.* 60 (11) 174 (1981); Groggins, op. cit., p. 523.

<sup>21</sup>Groggins, op. cit., p. 60 ff.; Albright and Hanson (eds.), *Industrial and Laboratory Nitrations*, ACS, Columbus, Ohio, 1975.

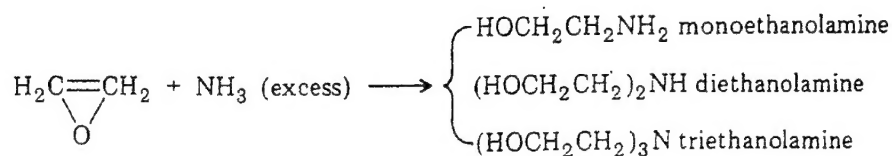


since the turn of the century, particularly for the manufacture of explosives. Nitrobenzene (Chap. 39) is probably the most important nitration product. Certain esters of nitric acid (cellulose nitrate, PETN, glyceryl trinitrate) are often referred to as nitro compounds (nitrocellulose, nitroglycerin), but this terminology should be avoided.

**Nitroparaffins.**<sup>22</sup> Vapor-phase nitration of paraffin hydrocarbons, particularly propane, can be brought about by uncatalyzed contact between a large excess of hydrocarbon and nitric acid vapor at around 400°C, followed by quenching. A multiplicity of nitrated and oxidized products results from nitrating propane; nitromethane, nitroethane, nitropropanes, CO<sub>2</sub>, etc., all appear, but yields of useful products are fair. Materials of construction must be very oxidation-resistant and are usually of ceramic-lined steel. The nitroparaffins have found limited use as fuels for race cars, submarines, and model airplanes. Their reduction products, the amines, and other hydroxy compounds resulting from aldol condensations have made a great many new aliphatic syntheses possible because of their ready reactivity.

**AMINATION.**<sup>23</sup> Amination, or reaction with ammonia, is used to form both aliphatic and aromatic amines. Reduction of nitro compounds is the traditional process for producing amines, but ammonia or substituted ammonias (amines) react directly to form amines. The production of aniline by amination now exceeds that produced by reduction (of nitrobenzene), Chap. 39.

**Ethanolamines** have been found to be very useful, for the alkalinity of the compounds varies with the degree of substitution, making a wide range of properties available from their salts. An equilibrium mixture of the three amines results when ethylene oxide is bubbled through 28% aqueous ammonia at 30 to 40°C. By recirculating the products of the reaction, altering the temperatures, pressures, and the ratio of ammonia to ethylene oxide, but always having an excess of ammonia, it is possible to make the desired amine predominate. Diluent gas also alters the product ratio.



After the strongly exothermic reaction, the reaction products are recovered and separated by flashing off and recycling the ammonia, and then fractionating the amine products. Demand for the individual amines swings quite widely, so the process must be kept flexible to meet changing needs.

**Methylamines** are made by reacting gaseous methanol with a catalyst at 350 to 400°C and 2 MPa, then distilling the reaction mixture. Any ratio of mono-, di-, or tri-methylamines is possible by recirculating the unwanted products. In 1981,  $102 \times 10^6$  kg of methylamines were consumed in the United States. Monomethylamine is used in explosives, 40 percent; insecticides, 33 percent; and surfactants, 8 percent. Dimethylamine is used for the manufacture of dimethylformamide and acetamide, 40 percent; pesticides, 14 percent; and water

<sup>22</sup>Bachmann and Pollack, *Ind. Eng. Chem.* 46 715 (1954); Albright, Nitration of Paraffins. *Chem. Eng.* 73 (12) 149 (1966).

<sup>23</sup>Ramiouille and David, Improved Methylamine Process, *Hydrocarbon Process.* 60 (7) 113 (1981).

treatment, 13 percent. Trimethylamine is used to form choline chloride, 70 percent, and to make biocides and slimicides, 20 percent.

Other alkylamines can be made in similar fashion from the alcohol and ammonia. Methyl, ethyl, isopropyl, cyclohexyl, and combination amines<sup>24</sup> have comparatively small markets and are usually made by reacting the correct alcohol with anhydrous ammonia in the vapor phase.

**OXIDATION.** Controlled oxidation is a valuable conversion method. The problem is to stop the reaction short of full combustion to CO, CO<sub>2</sub>, and water. Usually it is desired to break C—H or C—C bonds and replace them with C—O bonds. The most readily available oxidant is air, but it contains a large quantity of unreactive nitrogen to carry away much heat and dilute the products, making their recovery more difficult. In a few rare cases, ozone is the preferred form of oxygen. Most oxygen has been separated from air, and the steel industry is the largest consumer, but the chemical industry consumes several thousand metric tons per day. Sittig points out that oxygen is often cheaper than air, largely because of increased yields, reduced recycle intervals, higher reaction rates, reduced equipment size, and reduced heat loss to nitrogen. Both liquid- and vapor-phase reactions are used industrially. All oxidation reactions are extremely exothermic, so heat removal can be a major problem. The commonest catalyst is V<sub>2</sub>O<sub>5</sub>, which becomes effective at about 400°C.

The Celanese Corporation has large plants at Bishop and Pampa, Tex., which oxidize propane and butane, separately or in LPG mixtures, to yield a variety of oxygen-containing chemicals. Better production has resulted from the use of oxygen, replacing air. Products produced include acetic acid, acetic anhydride, acetaldehyde, formaldehyde, acetone, butyraldehyde, ethyl acetate, butanol, and vinyl acetate. The cost of separating such mixtures forms an appreciable part of the cost of production. Catalyst selection for LPG oxidation gives some control over the product obtained. For example, liquid-phase oxidation of butane at 175°C and 5.5 MPa with a cobalt catalyst yields 60 percent acetic acid and 6 percent formic acid. Substitution of a manganese catalyst gives 62 percent acetic and 23 percent formic.

*Phenol* is currently made by two processes, both involving oxidation. The major process, through oxidation of cumene to cumene hydroperoxide, followed by decomposition to phenol and acetone is described in Chap. 34. A small amount of phenol is also made by the oxidation of toluene to benzoic acid, followed by decomposition to phenol.

*Benzoic acid* is synthesized to the extent of  $382 \times 10^6$  kg/year. Most (54 percent) goes into phenol production, but significant amounts are used to make plasticizers, benzoyl chloride, sodium benzoate, and butyl benzoate. All U.S. producers use liquid-phase toluene oxidation over a cobalt naphthenate catalyst with air as the oxidizing agent. An older process<sup>25</sup> involving halogenation of toluene to benzotrichloride and its decomposition into benzoic acid is still used abroad.

*Maleic acid* and anhydride are recovered as by-products of the oxidation of xylenes and naphthalenes to form phthalic acids and are also made specifically by the partial oxidation of benzene over a V<sub>2</sub>O<sub>5</sub> catalyst. This is a highly exothermic reaction, and several modifications of the basic process exist<sup>26</sup> including one using butylenes as the starting materials.

Partial oxidation is also used to raise the temperature and thus bring about the decompo-

<sup>24</sup>Combination Amines, *Hydrocarbon Process.* 60 (11) 146 (1981).

<sup>25</sup>Lowenheim and Moran, *op. cit.*, p. 138.

<sup>26</sup>Wohlfahrt and Emig, Compare Maleic Anhydride Routes, *Hydrocarbon Process.* 59 (6) 83 (1980).